1.0

2.8
2.5
3.2
2.2
3.6
2.0
1.8

1.1

1.25
1.4
1.6

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

SUMMARY

ANNUAL REPORT

POLYCYCLIC HIGH ENERGY OXIDIZERS

Period Covered: 1 March 1981 through 28 February 1982

Prepared for: The Office of Naval Research
Dr. R. Miller Contract Monitor

Contract N00014-81-C-0204

March 1982

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POLYCYCLIC HIGH ENERGY OXIDIZERS

by

J. C. Hinshaw

A report on work sponsored by the
Office of Naval Research

Contract N00014-81-C-0204

March 1982

Thiokol/Wasatch Division
P.O. Box 524
Brigham City, Utah 84302

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Polycyclic Oxidizers   tris(acylamino)methanes
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Nitramines

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Efforts toward the synthesis of polycyclic high density, high energy oxidizers have involved examination of synthetic paths to the hexaazaadamantane framework. Routes examined include condensation of amides with an orthoformate, reaction of tris(acylamino) methanes with orthoformate and cyclizations based on acylated perhydrotriazines. The cyclization chemistry of a pentaazabicyclononadiene is also under investigation.

20. Abstract (continued)

Several routes to tetranitrazabicyclooctane ("bicyclic HMX") have also been examined including modification of the preformed tetraazabicyclooctane ring system and cyclization approaches.

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CONTENTS

INTRODUCTION

The object of this program has been to synthesize and evaluate new high density, high energy, polycyclic nitramine/nitro containing oxidizers for solid propellant/explosive applications.

TECHNICAL DISCUSSION

A direct approach to the development of new high energy propellants with improved ballistic characteristics involves the design, synthesis, and development of new high energy oxidizers as HMX/RDX replacements. The ideal HMX/RDX alternative would incorporate many physical properties superior to HMX/RDX in addition to providing propellant compositions with much improved ballistic flexibility.

In considering compounds for potential use as new high energy oxidizers, we have selected organic compounds having a minimum of hydrogen (favors less water formation in propellant combustion products for minimum signature exhaust applications) and high $-NO_2$ functionality (favors high energy with a minimum loss in thermal stability). In addition, we propose to incorporate these features into symmetrical polycyclic structures. Such polycyclic structures incorporating energetic nitramine/nitro functionality are expected to yield the following improvements over presently available high energy oxidizers:

      1. Increased energy

      2. Increased density

      3. Improved stability

      4. Latitude in ballistic tailoring

Synthesis

Compound I, N^1, N^2, N^3, N^4, N^5, N^6 -hexanitro-2,4,6,8,9,10-hexaazaadamantane.
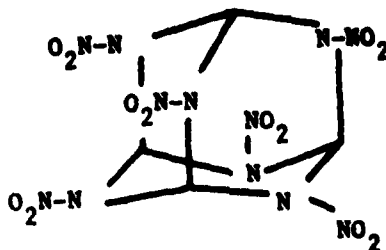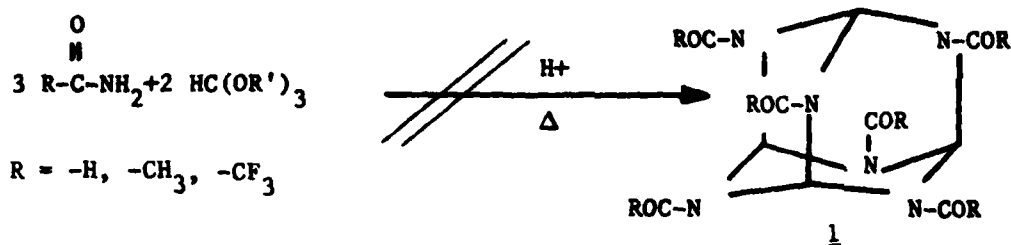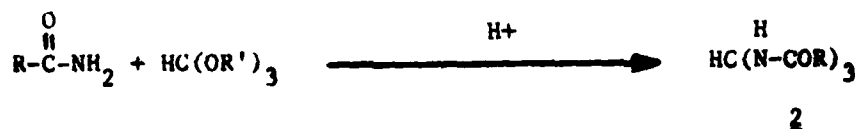

I

The hexaazaadamantane ring system remains unknown. We have examined several viable synthetic routes to the cage structure.

The direct synthesis (Scheme I) of a hexaazaadamantane starting from a number of different amides and a trialkyl orthoformate lead only to the corresponding tri(acylamino)methanes ($\underline{2}$)[1] (Scheme II).

SCHEME I

$$3 \ R\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2 + 2 \ HC(OR')_3 \quad \xrightarrow[\Delta]{H+} \!\!\!\!\!\!\!\!\!\!\!\! /\!/$$

$$R = -H, \ -CH_3, \ -CF_3$$

SCHEME II

$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2 + HC(OR')_3 \quad \xrightarrow{H+} \quad HC(\overset{H}{N}\text{-}COR)_3$$
$$\underline{2}$$
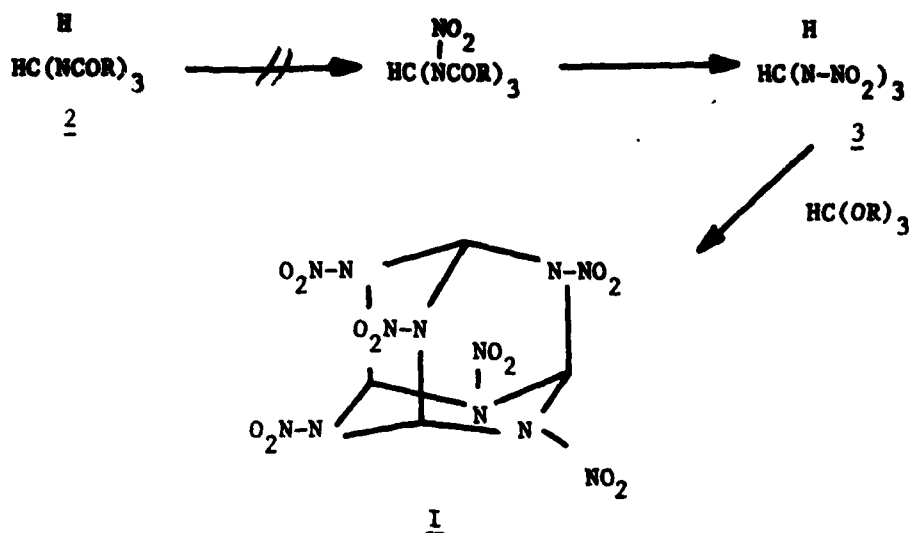
Attempts to force the reaction of Scheme I to the desired cage structure under conditions of higher temperatures and/or pressure lead only to unidentified black reaction mixtures. Similarly, reactions under forcing conditions using the tris(acylamino)methanes ($\underline{2}$) as starting materials were unfruitful.

In an alternate route, (Scheme III) nitration of the tris(acylamino) methanes $\underline{2}$ followed by hydrolysis[2] was expected to lead to the unknown tris(nitramino)-methane $\underline{3}$, an interesting high energy substance in its own right. Reaction of $\underline{3}$ with an orthoformate may lead directly to $\underline{I}$.

Scheme III

$$\text{HC(NCOR)}_3 \xrightarrow{\;\;//\;\;} \overset{\overset{\displaystyle NO_2}{|}}{\text{HC(NCOR)}_3} \xrightarrow{\hspace{2cm}} \overset{\overset{\displaystyle H}{}}{\text{HC(N-NO}_2)_3}$$

$$\underset{\underline{2}}{} \hspace{4cm} \underset{\underline{3}}{}$$

$$\text{HC(OR)}_3$$

$$\underline{I}$$

However, attempted nitration of tris(acetamido)methane $\underline{2}$ (R = -CH$_3$) under standard conditions (nitric acid/acetic anhydride) resulted in complete destruction of starting material and the isolation of no organic products. We are presently attempting to follow this reaction by NMR in order to ascertain the course of the nitration.

A less direct route (Scheme IV) to acylated azaadamantane $\underline{1}$ was examined.

Reduction of aromatic rings including pyridines and pyrimidines via hydrogenation over rhodium or platinum catalysts is well known[3,4]. However, reports of hydrogenation of triazine rings are lacking although saturation of the acylated melamine $\underline{4}$ under similar conditions in the presence of acetic anhydride to trap and stabilize the intermediate perhydrotriazine as acylated derivatives $\underline{5}$ appeared viable.

Attempts to hydrogenate triacetylmelamine $\underline{4}$ (R = -CH$_3$) to the desired saturated intermediate were frustrated by the pronounced insolubility of the compound.

SCHEME IV

$R = -CH_3, -C_2H_5,$.

Tripropionylmelamine($\underline{4}$, R=-C_2H_5) was successfully prepared in an attempt to secure a more soluble acylated melamine derivative for attempted catalytic hydrogenation of the triazine ring.

Unfortunately $\underline{4}$ (R=-C_2H_5) is not appreciably more soluble than the acetyl derivative. Consequently, hydrogenation at room temperature and 50 psi hydrogen over Rh-Pt catalyst resulted in no hydrogen uptake even after many days. High pressure and high temperature (up to 1200 psi, 185°C) hydrogenation conditions resulted in destruction of starting material and the production of dark colored amine smelling residues from which no identifiable materials have yet been isolated.

The bis-trifluoroacetate $\underline{6}$ of melamine was easily prepared and proved quite soluble in the desired acetic acid/acetic anhydride hydrogenation solvent.
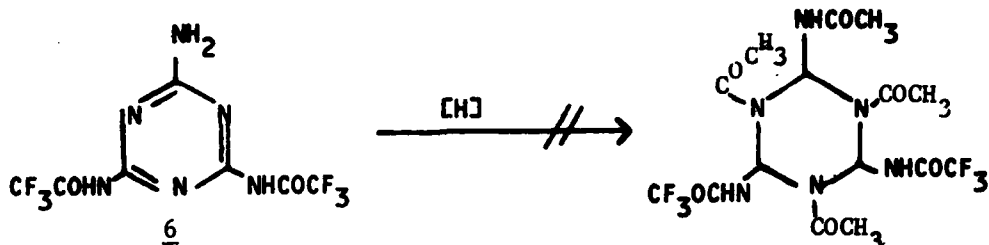

However, even prolonged room temperature low pressure hydrogenation of $\underline{6}$ over Rh-Pt resulted again in no hydrogen uptake. Some evidence for the incorporation of acetyl group into the starting material (acetyl-trifluoroacetyl exchange?) was noted under these reaction conditions.

Subsequently it was found that tripropionyl melamine $\underline{4}$ $(R=-C_2H_5)$ was soluble in warm trifluoroacetic acid/trifluoroacetic anhydride. However, prolonged low pressure hydrogenation of $\underline{4}(R=-C_2H_5)$ over Rh-Pt in this solvent system resulted again in no hydrogen uptake. This route to the hexaazaadamantane ring system has been abandoned.

In an alternate, new approach (Scheme V) we examined the construction of desired tricyclic azaadamantane system $\underline{7}$ from the available pentaaza-bicyclo(3.3.1)nonadiene $\underline{8}$ $(R=-H).$[6]

SCHEME V
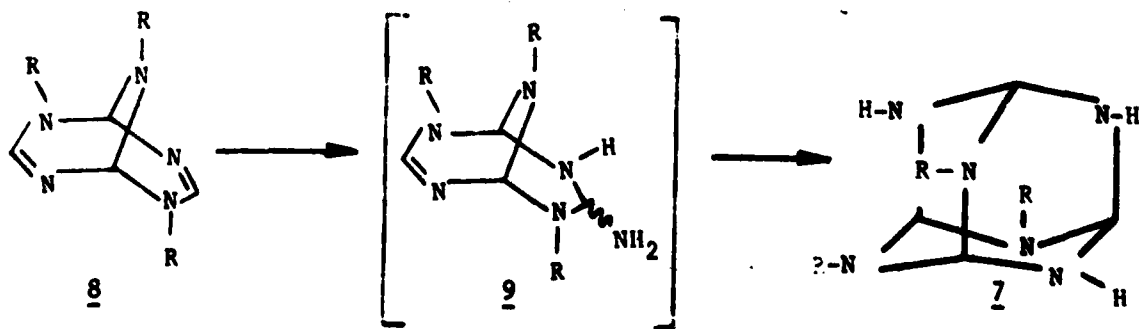
Thus, addition of ammonia to one amidine linkage i: 8 was expected to
lead to 7 via cyclization of 9. Similar synthetic schemes have been used
to prepare heteroadamantanes 10 starting from the carbocycle 11[5].

11   10   X = O, N-R, S
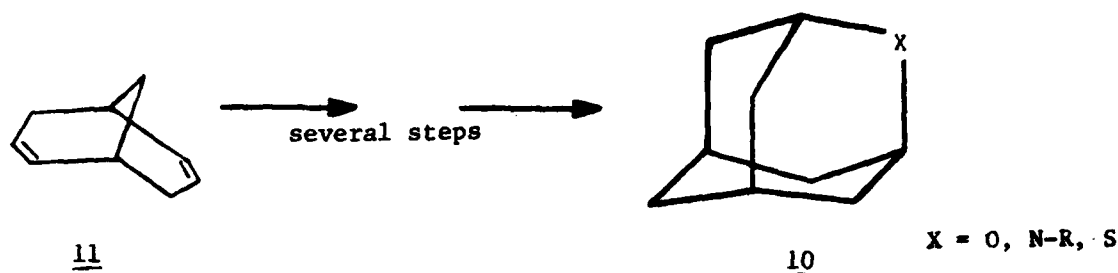
However, from the onset, we were concerned that ammonia addition to
bicycle 8 would occur from the exo side by analogy with the well known
chemistry of many carbobicyclic systems. The resulting stereochemistry
would then, of course, be unfavorable for the desired cyclization to 7.

Indeed refluxing pentaazabicyclononadiene, prepared by the literature
procedure[6], with aqueous ammonia gave a mixture whose mass spectrum was
characterized by a large peak at M/z = 140. Although the proton NMR of the
reaction mixture consisted only of unresolved broad absorptions, the M/z = 140
peak was attributed to the formation of the exoamine adduct 12.

MW = 142   MW = 140

12
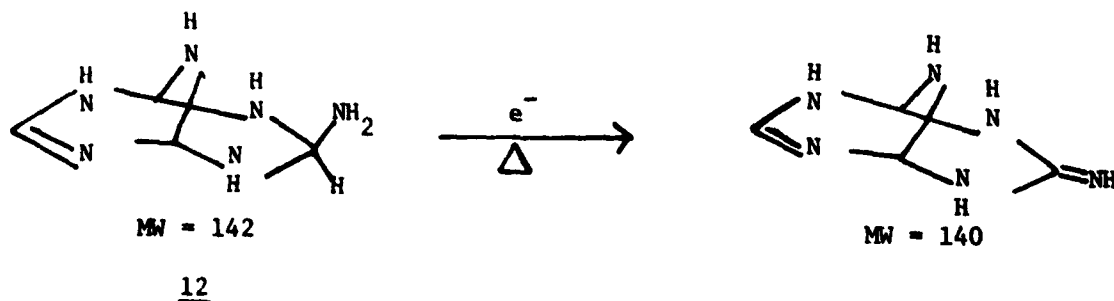
The proposed thermal and/or electron impact induced oxidation of the trisaminomethane functionality in 12 was thought consistant with the facile oxidation exhibited by a number of recently reported trisaminomethane derivaties.[7]

Consequently, we carried out a series of oxidation, reduction reactions designed to convert the presumed exo-adduct 12 into the desired endo adduct 13.
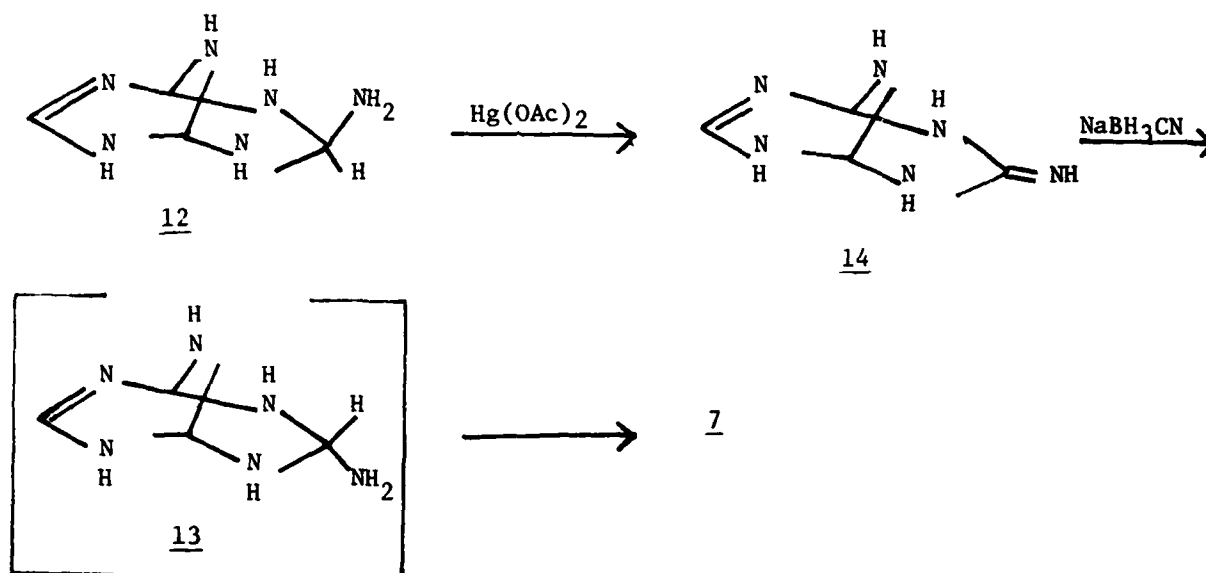

Oxidation of 12 with mercuric acetate[8] followed by reduction with a limited amount of sodium cyanoborohydride was expected to lead to endo 13 via exo delivery of hydride to guanidine 14. Indeed examination of the proton NMR spectrum of the crude product (isolated as the picrate) after carrying out the indicated oxidation reduction sequence showed a sharp singlet (non-exchanging with D_2O) at 5.0 δ (acetone d_6) or 4.65 δ (DMSOd_6). This observation was consistent with the formation of the desired hexaazaadamantane 7 via spontaneous cyclization of endo 13. The mass spectrum of the product was characterized by a strong peak at M/z 140 which, it was felt, was consistent with the desired product 7 via the following electron impact induced rearrangement/oxidation:
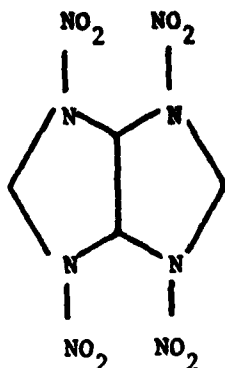
MW 142 MW 142 MW 140
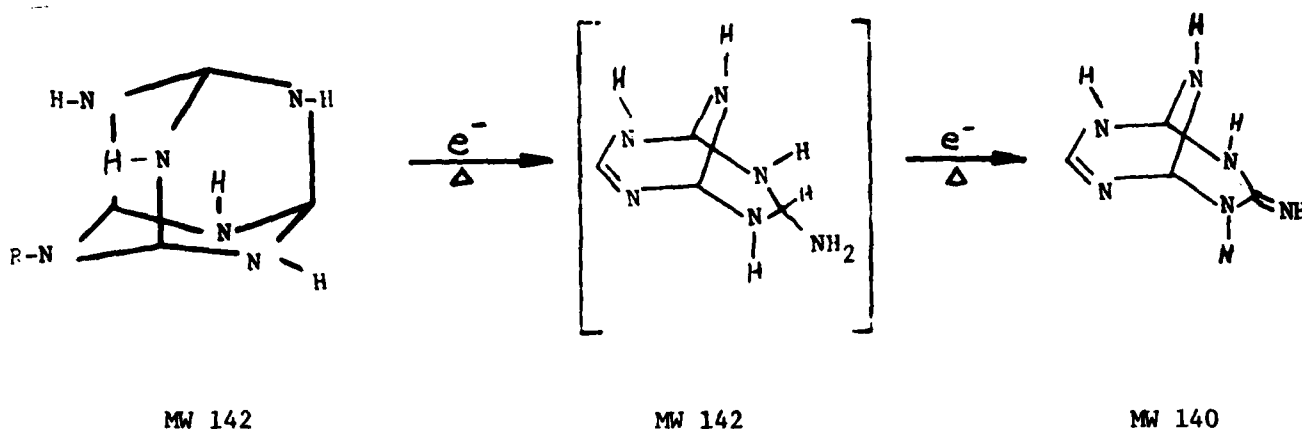
The ^{13}CNMR spectrum of the product showed one resonance at 72.7 ppm a somewhat higher field absorption than that expected for a trisaminomethane derivative. However, an off resonance decoupled ^{13}CNMR experiment showed conclusively that the unique carbon resonance at 72.7 ppm was attached to two hydrogens ($>CH_2$) clearly inconsistent with the desired polycycle 7.

Subsequently it was found that prolonged treatment of pentaazabicyclo-nonadiene 8 with *aqueous ammonia* led directly to this unknown product. The substance was finally isolated and identified as the tetraazaadamantane 15 (hexamine).

15
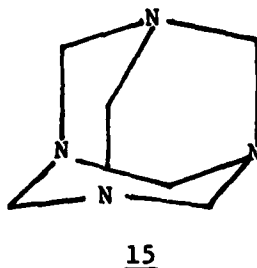
Closer examination of the pentazabicyclononadiene starting material as prepared by the literature method[6] revealed that the material is apparently mostly polymeric with only trace quantities of the desired azabicycle 8 present. Currently we believe hexamine (15) arises from ammonia reacting with formaldehyde supplied from this polymer mixture. Current studies are directed toward (1) attempted isolation of the pentaazabicyclononadiene from this literature reaction and (2) attempts to prepare 8 in a more pure form by alternate synthetic routes.
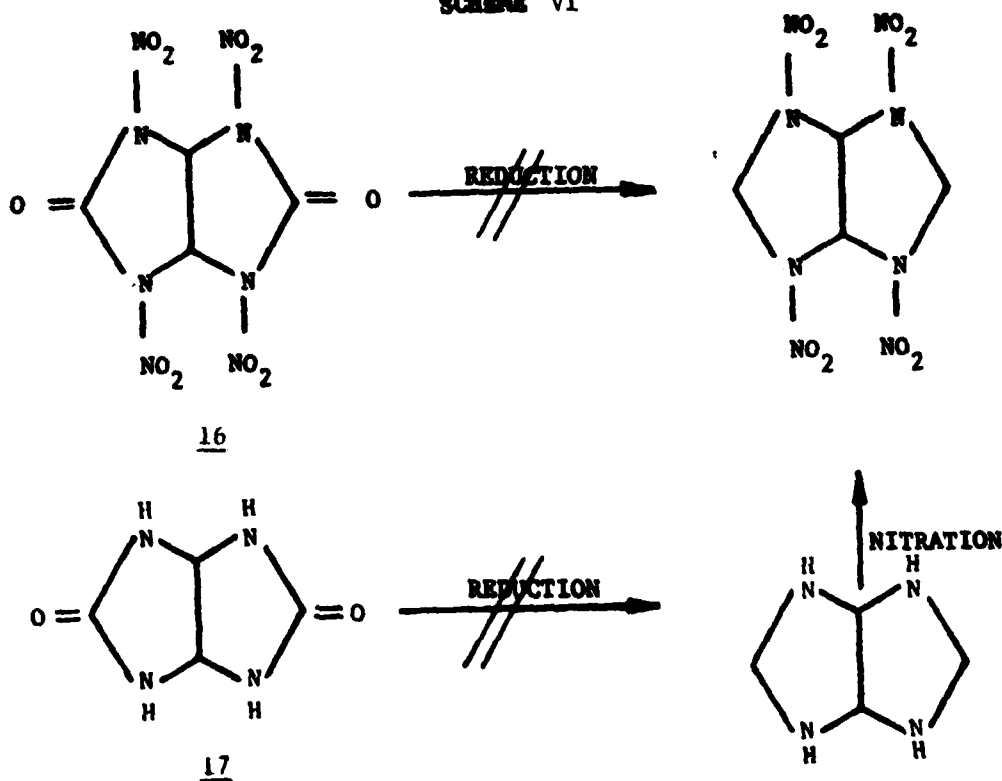
Compound II, N^1,N^2,N^2,N^4-Tetranitro-2,4,6,8-tetraazatricyclo (3.3.0) octane ("Bicyclic HMX").

NO_2   NO_2

[structure of compound II with four NO_2 groups on a bicyclic tetraazatricyclo ring system]

NO_2   NO_2

II

We have examined a number of synthetic routes to II. To date, direct reduction (Scheme VI) of either tetranitroglycoluril **16** or glycoluril **17** under a variety of conditions (BH_3/THF, $LiAlH_4$, diisobutylaluminum hydride, $NaBH_4$/CF_3COOH, etc.) to the desired bicyclic ring systems has proven unsuccessful.

SCHEME VI

[Scheme VI showing reduction reactions: compound 16 (tetranitroglycoluril with two C=O groups) undergoing REDUCTION (crossed out) to form II; compound 17 (glycoluril with NH groups and two C=O groups) undergoing REDUCTION (crossed out) to form a bicyclic ring system which could undergo NITRATION to form II]

16

17

-9-

However, in a model experiment, tetramethylglycoluril 18 (R = -CH$_3$) was successfully reduced to 19 (R = -CH$_3$).


18   19
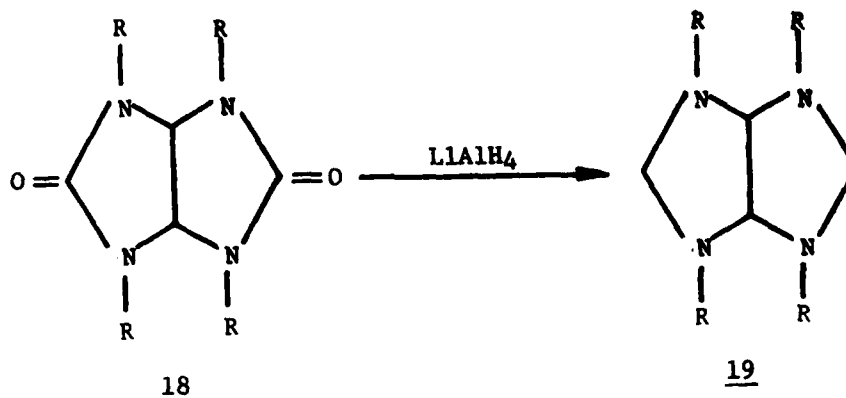
Experiments were then undertaken to prepare analog 19 (R = -CH(CH$_3$)$_2$) which was expected to lead to II by dealkylative nitrolysis.[9]

Tetraisopropylglycoluril 18 (R = CH(CH$_3$)$_2$) has been successfully prepared, albeit in low yield, from diisopropylurea and glyoxal. Reduction with LiAlH$_4$ gave an oil the mass spectrum of which showed evidence for the presence of the desired intermediate 19 (R = -CH(CH$_3$)$_2$).

However, considerable work modifying reaction conditions and examination of a number of reducing agents has so far been unfruitful in enabling us to obtain sufficient quantities of 19 (R=-CH(CH$_3$)$_2$) for further experimentation. Attention was therefore directed toward alternate synthetic routes to the tetraazabicyclo (3.3.0) octane ring system. For example, the condensation of methylenediamine[10] with glyoxal was examined in an attempt to construct directly the parent ring system.


+ H$_2$NCH$_2$NH$_2$ ⟶ ?
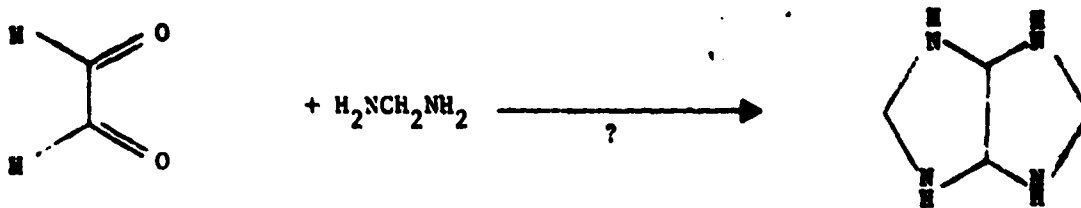
Initial experiments have so far been unsuccessful although a similar condensation with ethylenediamine and glyoxal was used to prepare 20.[11]

$$
\begin{array}{c}
\text{20}
\end{array}
$$
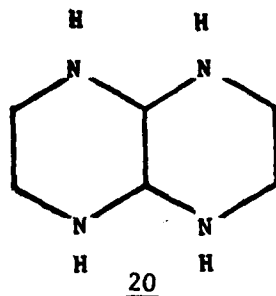
Further experimentation with this reaction sequence is underway. Also reaction of glyoxal with both methylenebisacetamide and methylene dinitramine[2] is being examined.

We have recently prepared tetranitraminoethane 21[12] and plan to examine its reaction with formaldehyde as an alternate condensation approach to II.

$$
\text{21} \qquad +2 \ CH_2O \xrightarrow{?} II
$$
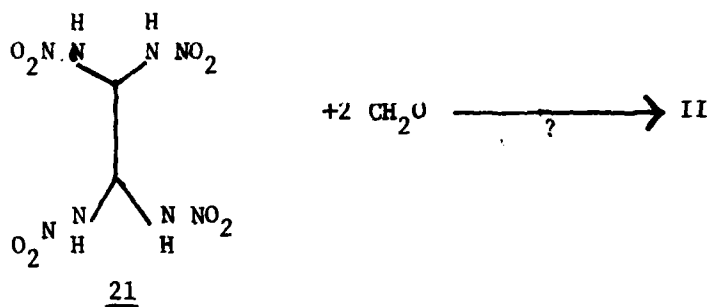
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1) H. Bredereck, G. Gompper, H. Rempfer, K. Klem, and K. Keck, Chem. Ber., 92, 329 (1959).

2) An analogous procedure is used to prepare methylenedinitramine from methylenebisacetamide, R. C. Brian and A. H. Lamberton, J Chem Soc, 1633 (1949). See also: Rocketdyne, Interim Final Report, R-6513, Aug 1966, Contract NAS7-293.

3) P. N. Rylander, "Catalytic Hydrogenation in Organic Synthesis," Academic Press, New York, 1979, Chap 11 and 12.

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5) R. C. Fort, Jr., "Adamantane, the Chemistry of Diamond Molecules," Studies in Organic Chemistry Series, Vol 5, P. G. Gassman Ed., Marcel Dekler Inc., New York, 1976.

6) Netherlands Patent, 6,500, 521; see Chem Abstracts, 64 2116a (1966).

7) J. M. Erhardt and J. Wuest, J. Amer. Chem. Soc., 102, 6363 (1980). T. Atkins, J. Amer. Chem Soc., 102, 6364 (1980). J. M. Erhardt, E. Grover, and J. Wuest, J. Amer. Chem. Soc., 102, 6365 (1980).

8) N. J. Leonard and D. F. Morrow, J. Amer. Chem. Soc., 80, 371 (1958).

9) Dealkylative nitrolysis procedures, private communication from H. Adolph, Naval Surface Weapons Center, White Oak, Silver Spring, MD.

10) J. H. Grimes, R. G. Hannis, and A. J. Huggard, J. Chem Soc, 266 (1964).

11) R. L. Willer, Naval Weapons Center, Final Report TP 6303, Aug 1981.

12) P. Zhongji and W. Daozheng, Acta Armamentaii, 3 (3), 23 (1980).

Appendix

Theoretical Performance Calculations On New High Density, High Energy
Polycyclic Oxidizers

Using estimated densities[1] and heats of formation[2,3] theoretical
performance calculations have been carried out for a number of our target
polycyclic high energy oxidizers in several propellant formulations. The
results of these calculations are tabulated and they show the considerable
improvements in propellant Isp and propellant densities that are expected
from the application of these new materials.

1) Estimated densities were calculated by the method of D. Cichra, J. Holder,
    and C. Dickinson, "Estimation of "Normal" Densities of Explosive
    Compounds from Empirical Atomic Volumes," NSWC Report TR 79-273,
    12 February 1980.

2) Estimated heats of formation were calculated using a method developed
    by A. D. Little, Inc.,[3] and extended by Thiokol/Wasatch with corrections
    applied for ring strain energies.[4]

3) Calculation of Heats of Combustion of Organic Compounds From Structural
    Features, A. D. Little, Inc., Report, Contract DH19-020-ORD-47, May
    1952.

4) J. Gasteiger and O. Dammer, Tetrahedron, 34, 2939 (1978).

TABLE I

THEORETICAL DENSITIES AND HEATS OF FORMATION
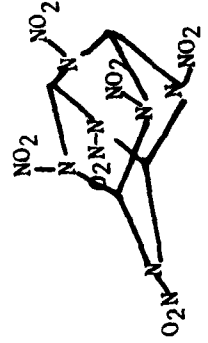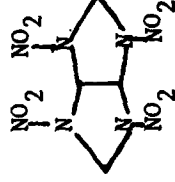### HIGH ENERGY OXIDIZERS

	HMX		
(structures)			
Density (g/cc)	1.9	2.3	2.0
ΔH_f (kcal/mole)	+18	+70	+37

TABLE II

THEORETICAL PERFORMANCE CALCULATIONS
HIGH ENERGY OXIDIZERS
MINIMUM SMOKE FORMULATION
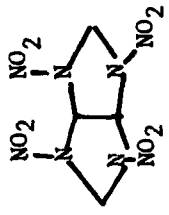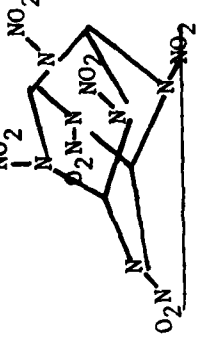
	Baseline		
I_{sp} (sec)	243.8	259.5	247.5
Density (lb/in^3)	0.0612	0.0681	0.0631

TABLE III

THEORETICAL PERFORMANCE CALCULATIONS
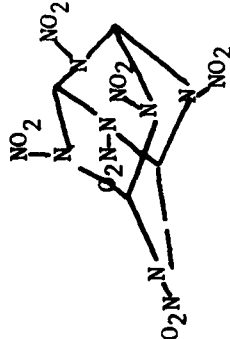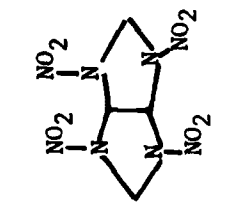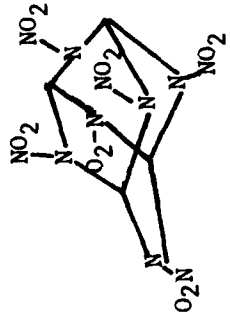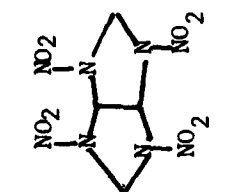HIGH ENERGY OXIDIZERS
TACTICAL FORMULATION

	Baseline		
Isp (sec)	270.5	270.8	271.2
Density (lb/in^3)	0.0675	0.0735	0.0682

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TABLE IV

THEORETICAL PERFORMANCE CALCULATIONS
HIGH ENERGY OXIDIZERS
STRATEGIC FORMULATION

	Baseline		
Isp (sec)	271.0	270.9	272.7
Density (lb/in^3)	0.0680	0.0752	0.0694